CEE 680 16 October 2012

FIRST EXAM

Closed book, one page of notes allowed.

Answer question #1 and #4, and either #2 or #3. Please state any additional assumptions you made, and show all work. You are welcome to use a graphical method of solution if it is appropriate.

Miscellaneous Information:

R = 1.987 cal/mole°K = 8.314 J/mole°K
Absolute zero = -273.15°C
1 joule = 0.239 calories
-20°C = wicked cold

1. (50%) You've been asked to make a mixed carbon standard solution for total organic carbon (TOC) and total inorganic carbon (TIC) analysis. To do this you add 1 mM of KHP (potassium hydrogen phthalate, $C_6H_4(COOH)COO^-K^+$) to a liter of water followed by 10 mM of sodium bicarbonate.

   a. Determine the pH and concentration of all soluble species in this solution? Approximate values (±0.2 log units) will suffice.
   b. What is the TOC of this solution in mg-C/L? What is the TIC of this solution in mg-C/L?
   c. You are then asked to acidify the solution by adding 11 mM of HCl. Determine the pH and concentration of soluble species after this last step.

a. Prepare Log C vs pH graph and write a proton balance

$$HPhth^-$$
$$HCO_3^-$$
$$[H_2Phth] + [H_2CO_3] + [H^+] = [OH^-] + [CO_3^{-2}] + [Phth^{-2}]$$

Which reduces to:

$$[H_2CO_3] = [Phth^{-2}]$$

For a pH of 7.3

$[H_2Phth]$ = 10^-9.2
$[HPhth^-]$ = 10^-4.8
$[Phth^{-2}]$ = 10^-3.0
$[H_2CO_3]$ = 10^-3.0
$[HCO_3^-]$ = 10^-2.1

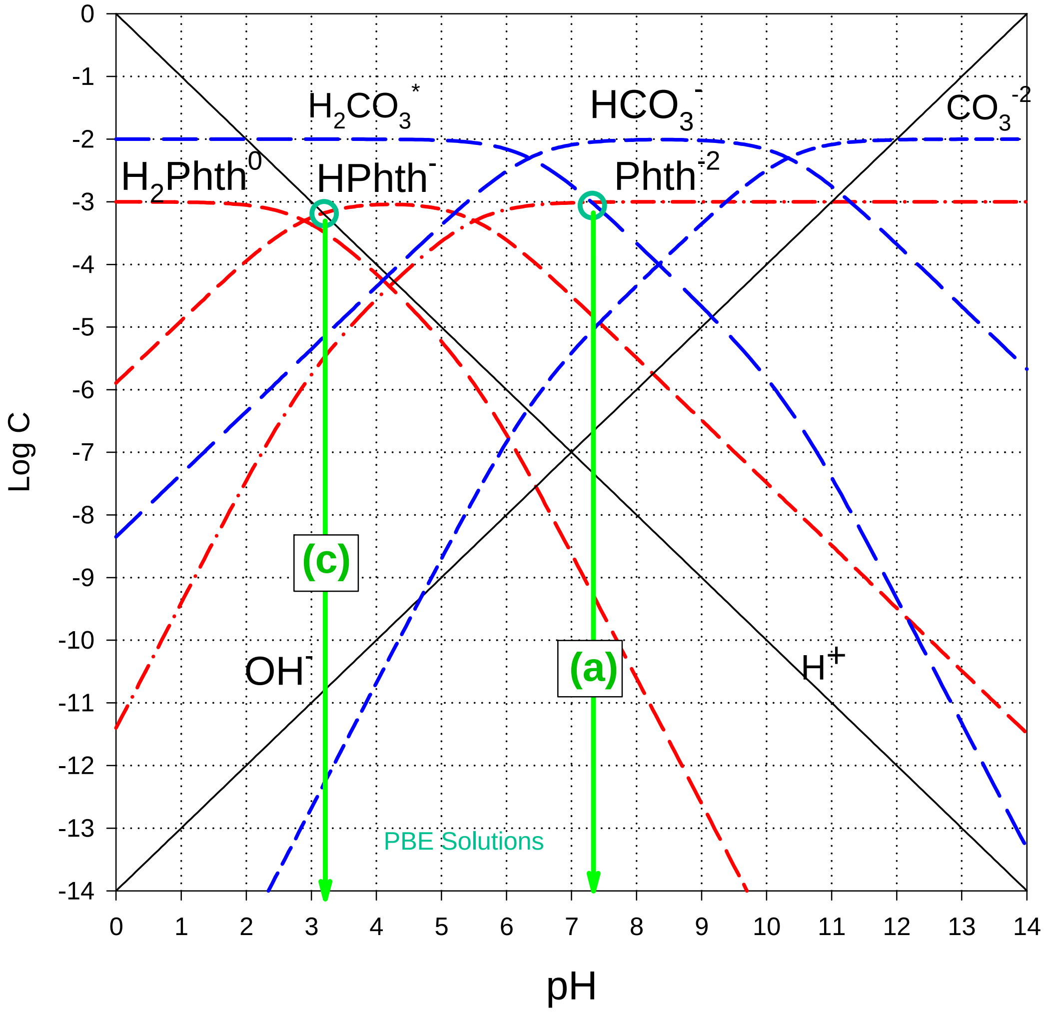
$[CO_3^{-2}]$ = 10^-5.1
$[H^+]$ = 10^-7.3
$[OH^-]$ = 10^-6.7
$[K^+]$ = 10^-2
$[Na^+]$ = 10^-3

Check assumptions: graphical comparison

b. Recognize that the phthalate is all organic carbon and the bicarbonate is inorganic

TOC = 1mM * (8C/mole) * 12mg-C/mM = **96 mg-C/L**

TIC = 10mM * (1C/mole) * 12mg-C/mM = **120 mg-C/L**



c. Now recognize that 11 mM is exactly what is needed to neutralize the protons in each of the two amphoteric additives, so you essentially have a pure solution of phthalic acid and carbonic acid. Now the proton balance is:

$$\begin{gathered} H_2Phth \\ H_2CO_3 \\ [H^+] = [OH^-] + [HCO_3^-] + [HPhth^-] + 2[CO_3^{-2}] + 2[Phth^{-2}] \end{gathered}$$

Which reduces to:

$$[H^+] = [HPhth^-]$$

For a pH of 3.2

$[H_2Phth] = 10$^-3.5
$[HPhth^-] = 10$^-3.2
$[Phth^{-2}] = 10$^-5.5
$[H_2CO_3] = 10$^-2.0
$[HCO_3^-] = 10$^-5.2
$[CO_3^{-2}] = 10$^-12.3
$[H^+] = 10$^-3.2
$[OH^-] = 10$^-10.8
$[Cl^-] = 1.1$x10^-2
$[K^+] = 10$^-2
$[Na^+] = 10$^-3

Check assumptions: graphical comparison

Answer either question #2 or #3, but not both

2. (40%) You have been asked to prepare a buffer at pH 6.0. The choices are an acetate buffer with a C_T of 5mM and carbonate buffer with a C_T of 2 mM. Which of the two will have a higher buffer intensity at the desired pH (i.e., at pH 6.0) under each of the following conditions? In answering this please show the calculated buffer intensity for both under each condition. Assume a closed system.

a. 25°C, I = 0
b. 25°C, I = 0.4

a. 25°C, I = 0

first calculate for the acetate buffer
recall that for a monoprotic acid, the buffer intensity is calculated from:

$$\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1\right)$$

and since this is a buffer problem, we can normally drop the hydroxide and hydrogen ion terms:

$$\beta \approx 2.303\left(C_T\alpha_0\alpha_1\right)$$

and substituting in for the alphas, we get:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{K_1}{[H^+]}}\right)\left(\frac{1}{\frac{[H^+]}{K_1}+1}\right)\right)$$

and for the particular pH of 6.0, this reduces to:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{10^{-4.75}}{10^{-6.0}}}\right)\left(\frac{1}{\frac{10^{-6.0}}{10^{-4.75}}+1}\right)\right)$$

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+10^{+1.25}}\right)\left(\frac{1}{10^{-1.25}+1}\right)\right)$$

$$\begin{aligned}\beta &\approx 2.303C_T\left(0.0532*0.947\right)\\ &\approx 0.1161C_T\end{aligned}$$

So that at 5 mM C_T, we have:

$$\beta \approx 0.1161(5x10^{-3}) \approx 0.000583$$

<u>next for the carbonate buffer</u>

recall that for a diprotic acid, the buffer intensity is calculated from:

$$\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2\right)$$

and since the pH is closest to the first pK, we can drop the second alpha term as well as the hydroxide and hydrogen ion terms:

$$\beta \approx 2.303\left(C_T \alpha_0 \alpha_1\right)$$

and substituting in for the alphas, we get:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}}\right)\left(\frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}}\right)\right)$$

and since $[H^+] >> K_2$, then we can simplify:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{K_1}{[H^+]}}\right)\left(\frac{1}{\frac{[H^+]}{K_1}+1}\right)\right)$$

and for the particular pH of 6.0, this reduces to:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{10^{-6.35}}{10^{-6.0}}}\right)\left(\frac{1}{\frac{10^{-6.0}}{10^{-6.35}}+1}\right)\right)$$

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+10^{-0.35}}\right)\left(\frac{1}{10^{+0.35}+1}\right)\right)$$

$$\begin{aligned}\beta &\approx 2.303C_T\left(0.691 * 0.309\right)\\ &\approx 0.492C_T\end{aligned}$$

So that at 2 mM C_T, we have:

$$\beta \approx 0.492(2x10^{-3}) \approx 0.000985$$

So, at 0.000985, **the carbonate buffer is stronger than the acetate buffer**

b. 25°C, I = 0.4

for both acid systems:

$$K_1 = \frac{[A^-]f_{A-}\{H^+\}}{[HA]f_{HA}} \quad \text{or} \quad \{H^+\} = \frac{[HA]}{[A^-]}\frac{f_{HA}}{f_A}K_1$$

Where f is the activity coefficient. And the mixed conditional constant would be

$$K_1{}' = \frac{[A^-]\{H^+\}}{[HA]} = K_1 \frac{f_{HA}}{f_{A-}}$$

And for uncharged HA, this term becomes unity and it simplifies to:

$$K_1{}' = \frac{K_1}{f_{A-}}$$

or

$$pK_1' = pK_1 + logf$$

Using the Davies equation: $\log f = -0.5(z)^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$

We get a non-zero log f for the anions, and they are the same for both bicarbonate and acetate.

$$\log f = -0.5(1)^2\left(\frac{\sqrt{0.4}}{1+\sqrt{0.4}} - 0.2*0.4\right) = -0.1537$$

And therefore, $f_{A-} = 0.70192$

So for acetate

$$pK_1' = 4.75 - 0.1537 = 4.596$$

And for carbonate

$$pK_1' = 6.35 - 0.1537 = 6.196$$

<u>Now, repeat what as was done in part a, but use the conditional pKs:</u>

So for acetate at the particular pH of 6.0, we now have:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{10^{-4.596}}{10^{-6.0}}}\right)\left(\frac{1}{\frac{10^{-6.0}}{10^{-4.596}}+1}\right)\right)$$

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+10^{+1.404}}\right)\left(\frac{1}{10^{-1.404}+1}\right)\right)$$

$$\beta \approx 2.303C_T\left(0.0380*0.962\right)$$
$$\approx 0.0841C_T$$

So that at 5 mM C_T, we have:

$$\beta \approx 0.0841(5x10^{-3}) \approx 0.000423$$

<u>next for the carbonate buffer</u>

recall that for we determined for the particular pH of 6.0:

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+\frac{10^{-6.196}}{10^{-6.0}}}\right)\left(\frac{1}{\frac{10^{-6.0}}{10^{-6.196}}+1}\right)\right)$$

$$\beta \approx 2.303\left(C_T\left(\frac{1}{1+10^{-0.196}}\right)\left(\frac{1}{10^{+0.196}+1}\right)\right)$$

$$\beta \approx 2.303C_T\left(0.611*0.389\right)$$
$$\approx 0.547C_T$$

So that at 2 mM C_T, we have:

$$\beta \approx 0.547(2x10^{-3}) \approx 0.00110$$

So, at 0.00110, **the carbonate buffer is still stronger than the acetate buffer**

3. (40%) At what pH is the molar concentration of H_3PO_4 and $H_2PO_4^-$ equal under each of the following conditions?

Note that the two species are equal when the pH = pK_a. Therefore it becomes an exercise in estimating pK_a under various conditions.

a. 25°C, I = 0

This is the standard condition where

$$pH = pK_a = 2.15$$

b. 100°C, I = 0

In this case you need to calculate the enthalpy of the reaction

$$\Delta H = -1.92$$

And then:

$$pH = pK_a = 2.43$$

c. 25°C, I = 0.25

Now the ionic strength corrections must be made and then:

$$pH = pK_a = 1.99$$

4. (10%) True/False. Mark each one of the following statements with either a "T" or an "F".

a. __**T**__ pH electrodes measure hydrogen ion activity rather than concentration

b. __**T**__ The Bronsted-Lowry definition of an acid is a substance that can donate a proton

c. __**F**__ Hardness is normally defined as the sum of all monovalent cations

d. __**F**__ Organic forms of carbon are those not bound to an oxygen atom.

e. __**T**__ Mass defects are directly proportional to nuclear binding energy

f. __**F**__ The alkalinity minus the acidity is equal to one-half the C_T (total carbonates)

g. __**T**__ Water forms cage-like structures that are due to hydrogen bonding between adjacent molecules

h. __**T**__ Increases in ionic strength have relatively minor effects on neutral species.

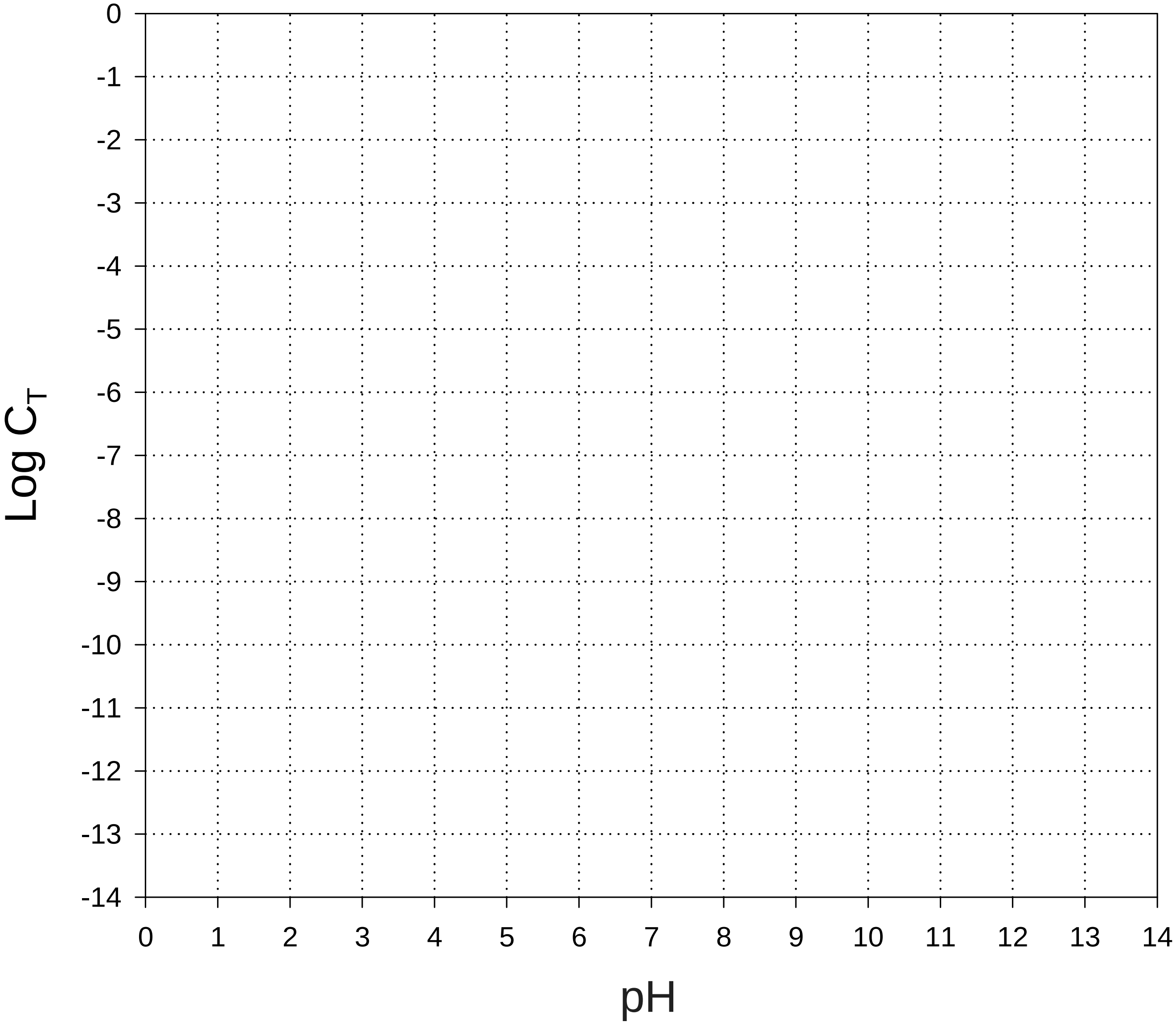
i. __**T**__ The standard assumption used for calculating the pH of a strong acid is that [A-] >> [HA].

j. __**T**__ The value of α_o plus α_1 must never exceed unity for any acid system.

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	0
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2,12.3)
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89 (&5.51)
Citric acid	$C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Aspartic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.06 (&9.92)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48 (&9.32)
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (&10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (&13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.32
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	14.00
Ammonia	$NH_3 = H^+ + NH_2^-$	23
Methane	$CH_4 = H^+ + CH_3^-$	34

Species	$\Delta\overline{H}_f^o$ kcal/mole	$\Delta\overline{G}_f^o$ kcal/mole
Ca^{+2}(aq)	-129.77	-132.18
$CaCO_3$(s), calcite	-288.45	-269.78
CaO (s)	-151.9	-144.4
C(s), graphite	0	0
CO_2(g)	-94.05	-94.26
CO_2(aq)	-98.69	-92.31
CH_4 (g)	-17.889	-12.140
H_2CO_3 (aq)	-167.0	-149.00
HCO_3^- (aq)	-165.18	-140.31
CO_3^{-2} (aq)	-161.63	-126.22
CH_3COOH	-116.79	-95.5
CH_3COO^-, acetate	-116.84	-89.0
H^+ (aq)	0	0
H_2 (g)	0	0
HF (aq)	-77.23	-71.63
F^- (aq)	-80.15	-67.28
Fe^{+2} (aq)	-21.0	-20.30
Fe^{+3} (aq)	-11.4	-2.52
$Fe(OH)_3$ (s)	-197.0	-166.0
NO_3^- (aq)	-49.372	-26.43
NH_3 (g)	-11.04	-3.976
NH_3 (aq)	-19.32	-6.37
NH_4^+ (aq)	-31.74	-19.00
HNO_3 (aq)	-49.372	-26.41
O_2 (aq)	-3.9	3.93
O_2 (g)	0	0
OH^- (aq)	-54.957	-37.595
H_2O (g)	-57.7979	-54.6357
H_2O (l)	-68.3174	-56.690
PO_4^{-3} (aq)	-305.30	-243.50
HPO_4^{-2} (aq)	-308.81	-260.34
$H_2PO_4^-$ (aq)	-309.82	-270.17
H_3PO_4 (aq)	-307.90	-273.08
SO_4^{-2}	-216.90	-177.34
HS^- (aq)	-4.22	3.01
H_2S(g)	-4.815	-7.892
H_2S(aq)	-9.4	-6.54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